Preparation and Thermal Analysis of Sn-Ag Nano Solders

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In this study, Sn-Ag nano solders of three different compositions (Sn-1.0 mass%Ag, Sn-3.5 mass%Ag and Sn-6.5 mass%Ag) were synthesized via arc-discharge process. The properties of Sn-Ag nano solders were analyzed using X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDX), and Differential Scanning Calorimetry (DSC). Particle size relatively widely ranged from 10 nm to 340 nm. For Sn-1.0 mass%Ag and Sn-3.5 mass%Ag, average size was 200–240 nm, and that for Sn-6.5 mass%Ag was 40–50 nm with some extra-ordinary large particles of ~100 nm. The melting points of the prepared SnAg nano solders were examined with DSC at different heating rates 1 K, 3 K and 5 K/min. The congruent melting point of Sn-Ag nano solders was found to be 487 K.

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prepared with an induction melting furnace in an Ar atmosphere. The solidified samples weighted approximately 220 g (25-mm diameter, 8-mm height).

Figure 1 shows a schematic diagram of the arc discharge apparatus. The system consists of a power supply, an arc chamber, a particle collector and a gas distributor. A sample alloy was placed on a water-cooled copper anode plate in the center of the reaction chamber. The upper tungsten rod served as the cathode. The distance between the two electrodes can be controlled from outside during operation. Once a master alloy tabulate was placed at the center of the reaction chamber, it was sealed, evacuated, and introduced Ar gas with a pressure of 20 kPa. The electric voltage and current were 20–30 V and 20–90 A, respectively.

The arc discharge process was carried out for about 1~2 h, which generated large amount of ~ 100 g nano powders. The chamber was cooled under Ar gas for 2 h before collecting alloy nanoparticles on the inner surface of the chamber.

2.2 Analysis method

X-Ray Diffraction (18 kV, Rigaku Model D/MAX-2500V XRD) was used to study the crystal structure of SnAg alloy nanoparticles. Transmission Electron Microscope (TEM, Tecnai20, 200 kV), High Resolution Transmission Electron Microscope (HR-TEM, Tecnai20, 300 kV) and Field Emission Scanning Electron Microscope (FE-SEM, Hitachi S-4300, 30 kV) were used to observe the morphologies of the synthesized nanoparticles. TEM specimens were prepared by using ultrasound to disperse manufactured SnAg alloy nanoparticles in ethanol and then one drop of the SnAg alloy nanoparticles solution was placed onto a carbon film supported by copper grids. SEM specimens were prepared as the same way on a silicon wafer. Energy Dispersive X-ray spectroscopy (EDX) (Horiba EX-200) was used to analyze the composition of SnAg nanoparticle alloys. The melting temperature of the nanoparticles alloys were determined by mean of Differential Scanning Calorimetry (DSC). DSC analysis was firstly carefully calibrated with 99.999% purity Sn (Kojundo Chemical Laboratory). For DSC analysis, the nanoparticles were dispersed in alcohol and then the mixture was dropped into an alumina crucible. The analysis was performed at different heating rates of 1, 3, and 5 K/min in the temperature range of 303 to 623 K under N2 (99.999% purity) atmosphere.

3. Results and Discussion

3.1 EDX study

The compositions of the prepared nanoparticles are given in Table 1. It was found that the Ag concentrations of nanoparticles were slightly lower than that of mother alloys. Nevertheless, the compositions were close to the master alloy, so it is considered that the arc discharge method can fabricate SnAg nano solders with fairly well controlled composition.

3.2 X-ray diffraction (XRD) patterns of SnAg alloys

Figure 2 shows XRD patterns of the SnAg nanoparticle alloys. It is clear that prominent peaks in XRD patterns of SnAg nano alloys are attributed to Sn and Ag3Sn phases. Therefore, it is considered that the Ag3Sn phase was successfully alloyed. From the XRD patterns, oxides peaks were not investigated.

3.3 Transmission electron microscopic (TEM) study

Figure 3 shows the TEM and FE-SEM images of the prepared nanoparticles. From these images, it was found that spherically shaped nanoparticles were partially necked with each other. The observed size distribution of Sn-1.0 mass%Ag nanoparticles was between 80~280 nm. Few larger particles of approximately 300 nm were also investigated. The particle size distribution of Sn-3.5 mass%Ag was in the range of 100~340 nm. For these two samples, the average size was 200~240 nm. For Sn-6.5 mass%Ag alloy nanoparticles, some parts are approximately 100 nm, but most of them were in the range of 20~80 nm (average size was 40~50 nm). The particle size distribution and weight percentage of all samples were shown in Fig. 4.

In order to verify the structure of SnAg nanoparticles manufactured by arc discharge process, the line-analysis was carried out. Figure 5 shows the line analysis result of a Sn-6.5 mass%Ag nanoparticle with a HR-TEM image. The Ag peak was only detected in a certain region with the Sn peak in the nanoparticle, which supports the existence of the Ag3Sn phase in the Sn matrix. Accordingly, it is considered that Ag3Sn and Sn phases were simultaneously formed during the arc discharge process. From the HR-TEM image, it is considered that the surface was slightly oxidized, but could not be detected from the line analysis or XRD analysis.

3.4 Differential scanning calorimetry (DSC) study

Figure 6 shows the DSC results with Sn-3.5 mass%Ag samples with three different heating rates. The measured
onset points (melting starting points) and the second peak points (liquidus temperatures) were almost the same for the three different heating rates. From the DSC analysis result at a heating rate of 1 K/min, it was clearly observed that the main peak was composed of several small peaks. It might be related to the existence of many different sizes of particles, namely as the particle size increased the melting point increased. In addition, during heating, small particles might be coagulated to larger particles. The sequence of coagulation of small particles is of interest, but not so easy to investigate. Additional research is required on the coagulation in the future work. Nevertheless, the second peak is located on the same position regardless of the heating rate. Therefore, when the particle grew to a certain size, the growth rate was considered to become slower, yielding the same liquidus temperature. Figure 7 shows the DSC results of the three samples at the same heating rate of 1 K/min. For comparison the DSC results of bulk samples were shown together. The measured melting temperatures of SnAg nanoparticles and bulk alloys were summarized in Table 2.

Using the present experimental results, a schematic phase diagram of Sn-Ag alloy nanoparticles at the Sn-rich corner was visualized in Fig. 8. It is clearly found that the melting point was decreased by $6-7 \, \text{K}$ from the bulk alloy. Mostly interesting result is that for Sn-3.5 mass%Ag nanoparticle a liquidus point was investigated, which was much higher than the bulk eutectic temperature. Therefore, it was expected that the eutectic composition was shifted for nanoparticles. From the phase diagram, it was likely that the eutectic composition was shifted to the Sn rich corner as suggested in our theoretical study.$^{13}$

Fig. 2 XRD analysis of the prepared nanoparticles: (a) Sn-1.0 mass%Ag, (b) Sn-3.5 mass%Ag, (c) Sn-6.5 mass%Ag.

Fig. 3 SEM and TEM images of the prepared nanoparticles: (a) SEM image of Sn-1.0 mass%Ag, (b) SEM image of Sn-3.5 mass%Ag, (c) TEM image of Sn-6.5 mass%Ag.
4. Conclusions

In the present study, we prepared three Sn-Ag nano solders (1.0, 3.5 and 6.5 mass%) by arc discharge process. The samples were analyzed by XRD, SEM, TEM, EDX and DSC. From the thermal analysis, it was found that the congruent melting point of Sn-Ag nanoparticles was decreased to 487 K. In addition, it was expected that the eutectic composition was shifted to the Sn rich corner.

Acknowledgements

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REFERENCES


Table 2 DSC peaks analysis results of the prepared nanoparticles and bulk alloys.

<table>
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<tr>
<th>Sample</th>
<th>Heating Rate</th>
<th>Onset Point (K)</th>
<th>Peak (K)</th>
<th>Offset Point (K)</th>
<th>Second Peak (K)</th>
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<tr>
<td>Sn-1.0 mass%Ag</td>
<td>1 K/min</td>
<td>486.2</td>
<td>489.6</td>
<td>497.2</td>
<td>502</td>
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<tr>
<td></td>
<td>3 K/min</td>
<td>485.9</td>
<td>490.8</td>
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<td></td>
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<tr>
<td></td>
<td>5 K/min</td>
<td>485.4</td>
<td>491.2</td>
<td>500.7</td>
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<tr>
<td>Bulk Solder</td>
<td>1 K/min</td>
<td>494.0</td>
<td>501.2</td>
<td>503.0</td>
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<td>Sn-3.5 mass%Ag</td>
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<td>487.1</td>
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<tr>
<td></td>
<td>3 K/min</td>
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<td>490.9</td>
<td>497.2</td>
<td></td>
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<tr>
<td></td>
<td>5 K/min</td>
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<td>493.2</td>
<td>499.3</td>
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<tr>
<td>Bulk Solder</td>
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<td>500.7</td>
<td>503.0</td>
<td>—</td>
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<tr>
<td>Sn-6.5 mass%Ag</td>
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<td>485.6</td>
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<td>539</td>
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<td>3 K/min</td>
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<td>494.0</td>
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<td></td>
<td>5 K/min</td>
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<td>494.0</td>
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<td>500.3</td>
<td>502.0</td>
<td>550</td>
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</table>

Fig. 7 The DSC analysis results of three different samples: (a) Sn-1.0 mass%Ag, (b) Sn-3.5 mass%Ag, (c) Sn-6.5 mass%Ag.

Fig. 8 A schematic illustration of the phase diagram of Sn-Ag system. (solid lines: bulk phase diagram, dashed lines: nano phase diagram)